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Catalytic Desulfurization of Dibenzothiophene and 4,6-Dimethyldibenzothiophene with Nickel Compounds

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*Summary: Catalytic amounts of the compounds $[(dippe)NiH]_2$ (**1**), $[(dcpe)NiH]_2$ (**2**), and $[Ni(PEt_3)_4]$ (**3**) (1−0.1 mol %) with alkyl Grignard reagents promoted the desulfurization of dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene, to produce the corresponding biphenyls (90−100%) in toluene or mixtures of biphenyls and thiols favored in THF. Also, the thianickelacycle $[(dippe)Ni(\eta^2\text{-}C,S\text{-}C_{12}H_8)]$ (**4**) was used as a catalyst precursor to test its participation as an active intermediary in the catalytic cycle.*

Introduction

The removal of sulfur from fuels is necessary for the reduction of pollution in the atmosphere by sulfur oxides.[1] The sulfur content in gasoline and diesel fuel will be reduced from the current levels of 300−500 ppm to meet the market limits in the United States of <30 ppm in 2006[2] and in Europe of <10 ppm by 2008.[3] Currently the desulfurization of petroleum feedstocks very much depends on catalytic hydrodesulfurization (HDS).[4] The commercial HDS process uses the cobalt- or nickel-doped molybdenum sulfide catalyst supported on alumina; however, the highest activity has been shown by platinum group metals, at least in model reactor studies, but they are not commercially used because of their higher cost.[5] Thus, a variety of organometallic compounds containing transition metals have been studied in homogeneous HDS reactions with thiophenes.[6] The less reactive thiophenes are dibenzothiophene (DBT) and its hindered analogues: those with alkyl groups in the 4 and 6 positions (4-RDBT and 4,6-R_2DBT), which constitute the bulk of the remaining sulfur compounds in petroleum fuels and must be removed in order to meet the above quoted environmental requirements.

It has been reported that transition metal-mediated C−S bond cleavage reactions take place for a variety of sulfur-containing molecules.[7] Of these, the reactions of Grignard reagents with thiophenes, benzothiophene, and DBT in the presence of nickel halide phosphine complexes (10 mol %) are of particular interest, as they give sulfur-free cross-coupling products, such as 2,2′-dimethy1,1′-biphenyl from DBT and methylmagnesium bromide.[8] A related report has recently appeared in which a variety of Ni(0) catalysts (3 mol %) mediated the formation of chiral 1,1′-binaphthyls in the asymmetric cross-coupling of dinaphtho[2,1-*b*:1′,2′-*d*]thiophene with the Grignard reagents and which has expanded the use of 1,9-disubstituted dibenzothiophenes.[9]

The use of organometallic nickel complexes in conjunction with other nucleophiles, like added hydride reagents, has been shown to desulfurize a variety of DBTs, affording the corresponding biphenyls as the organic products.[10] However, there are very few examples of structural characterization of the organometallic nickel fragments involved; the best examples in the field have been reported by Vicic and Jones,[11] using nickel(0) compounds, which were able to activate both C−S bonds of DBT and 4-MeDBT at room temperature and 4,6-Me_2DBT at 90 °C. All the reactions studied are stoichiometric reactions that yield several other organometallic compounds as well as the release of the corresponding biphenyls if a hydride, proton, or a hydrogen atom source is present. Very few compounds are known to ring open 4,6-Me_2DBT to yield desulfurization products, to the best of our knowledge none of them under catalytic conditions.[12−14b]

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Table 1. Nickel-Catalyzed Desulfurization with Grignard Reagents[a]

entry	complex (equiv)	thiophene (equiv)	Grignard (equiv)	solvent	organics (yield %)
1	**1** (1)	DBT (100)	MeMgBr (200)	toluene	MePh−PhMe (100)
2	**1** (1)	DBT (1000)	MeMgBr (2000)	toluene	MePh−PhMe (93), DBT (7)
3	**1** (1)	DBT (100)	MeMgBr (200)	THF	MePh−PhMe (60), MePh−PhSH (25), DBT (15)
4	**1** (1)	DBT (100)	MeMgBr (200)	mesitylene	MePh−PhMe (90), MePh−Ph (10)
5	**1** (1)	DBT (100)	^{i}PrMgCl (300)	toluene	Ph−Ph (70), ^{i}PrPh−Ph (30)
6	**4** (1)	DBT (100)	MeMgBr (200)	toluene	MePh−PhMe (91), DBT (9)
7	**2** (1)	DBT (100)	MeMgBr (200)	toluene	MePh−PhMe (76), MePh−Ph (5), DBT (19)
8	**3** (1)	DBT (100)	MeMgBr (200)	toluene	MePh−PhMe (100)
9	**3** (1)	DBT (1000)	MeMgBr (2000)	toluene	MePh−PhMe (100)
10	**3** (1)	4-MeDBT (1000)	MeMgBr (2000)	toluene	Me_2Ph−PhMe (100)
11	**1** (1)	4,6-Me_2DBT (100)	MeMgBr (300)	toluene	Me_2Ph−PhMe_2 (26), Me_2Ph−PhMe (2), 4,6-Me_2DBT (72)
12	**3** (1)	4,6-Me_2DBT (100)	MeMgBr (300)	toluene	Me_2Ph−PhMe_2 (46), Me_2Ph−PhMe (2), 4,6-Me_2DBT (51)
13	**3** (1)	4,6-Me_2DBT (50)	MeMgBr (150)	toluene	Me_2Ph−PhMe_2 (98), Me_2Ph−PhMe (2)
14	**3** (1)	4,6-Me_2DBT (100)	^{i}PrMgCl (300)	toluene	4,6-Me_2DBT (100)
15	none	4,6-Me_2DBT (100)	MeMgBr (200)	toluene	4,6-Me_2DBT (100)
16	**5** (1)	DBT (100)	MeMgBr (200)	toluene	MePh−PhMe (100)

[a] The reaction was carried out at reflux of the corresponding solvent, for 5 days, typically using approximately 0.058 mmol of the corresponding nickel catalyst. All yields were quantified by GC−MS after workup.

These results, along with our interest in metal-promoted HDS modeling studies,[14] encouraged us to explore the reactivity of [(dippe)NiH]$_2$ (**1**) and [Ni(PEt$_3$)$_4$] (**3**) with DBTs and Grignards to yield substituted biphenyls via a homogeneous catalytic desulfurization system that we report herein. Mechanistic insight for these desulfurizations is also provided.

The reactions were performed in a variety of conditions;[15] however the most relevant experiments are summarized in Table 1. In general, compounds **1**−**3** are able to desulfurize DBTs in good yields, complex **1** generates complex **4**, and compounds **2** and **3** might generate the analogue derivatives, with some important differences as follows.

Entries 1−9 are for DBT desulfurization when toluene or mesitylene is used in the presence of MeMgBr. The main products are the cross-coupling derivatives, i.e., methyl-substituted biphenyls in yields up to 90% for compounds **1** and **3**. The use of toluene instead of mesitylene was optimal, as the higher temperature required for refluxing mesitylene led to increased decomposition. The use of THF led repeatedly to the production of the corresponding thiol (MePh−PhSH) and to the recovery of DBT. Low yields are also obtained on using complex **2**, probably due to the bulky diphosphine. The result in entry 5, where ^{i}PrMgCl was used instead of MeMgBr, is noteworthy. Here biphenyl (Ph−Ph) was obtained in 70% yield along with the cross-coupled product (^{i}PrPh−Ph). One possible explanation of this result is that the initial attack of the nucleophile (^{i}Pr) occurs at the metal center, followed by a β-elimination.[16] This combination serves as an in situ source of "Ni−H" prior to the attack of the organic moiety that allows the release of biphenyl via a hydride migration, which can be envisaged as a product of an HDS process instead of a cross-coupling product. A similar pattern of reactivity was exhibited by 4-MeDBT (entry 10), the desulfurization being almost as easy as the case of DBT using Grignards.

Entries 11−14 display some of the results for 4,6-Me$_2$-DBT desulfurization. Here the reactivity of the catalytic system is a bit lower than the one observed with the analogous experiments using DBT, where a 0.1 mol % of nickel complex produced excellent yields of desulfurization. However, a total desulfurization of 4,6-Me2DBT can be achieved at 2 mol % of nickel complex. Here the use of ^{i}PrMgCl instead of MeMgBr did not allow any desulfurization or hydrodesulfurization at all (entry 14), which is probably due to steric restrictions.

To test the feasibility of the intermediacy of the corresponding thianickelacycles and nickelacycles during desulfurization, complexes **4** (entry 6) and [(dippe)-Ni(η^2-C,C'-$C_{12}H_8$)] (**5**) were prepared independently and used as catalyst precursors, leading to cross-coupling yields higher than 90%. By following the cross-coupling reaction of **4** by ^{31}P NMR we were able to verify that the main species formed in solution during the reaction are the ones identified by Vicic and Jones,[11] and all of them appear and disappear in a cyclic way, vide infra. During the entire course of the reaction, compounds **4**, **5**, [(dippe)$_2$Ni], and [(dippe)$_2$Ni$_2$(μ-S)] are observed. Besides the latter, other sulfur-containing species can be seen during the reaction such as [(dippe)Ni(μ-S)]$_2$ after 18 h and [(dippe)Ni(μ-S)]$_2$Ni(2,2′-biphenyl) after 96 h, all of them identified by their characteristic signals in ^{31}P{^{1}H} NMR.[17] Complex **4** reacts at room temperature on adding MeMgBr; it is re-formed during the reaction time under reflux and also remains at the end

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(15) A representative experiment was made as follows: In the drybox a 50 mL Schlenk flask was charged with [(dippe)NiH]$_2$ (0.0376 g, 0.058 mmol), dissolved in 8 mL of dry toluene, adding dibenzothiophene (1.0756 g, 5.838 mmol) with constant stirring during 30 min. After complete mixing and once the released gases had been vented in the box, a 1.4 M solution of MeMgBr (8.4 mL, 11.676 mmol) in toluene/THF (75:25) was added; the color changes to brown. The reaction mixture was heated to reflux under argon in a gas/vacuum line, constantly stirred for 5 days. During this time, a blend of precipitates can be seen: a beige precipitate and a red-brown precipitate. After this time the heating was stopped, and the sample was hydrolyzed at room temperature with HCl (10 mL, 10% v). A strong effervescence was observed with the immediate release of H_2S, which was usually bubbled into a trap with 50 mL of an aqueous concentrated solution of Pb(CH_3COO)$_2$. After bubbling and venting all the gases, the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was analyzed by GC−MS.

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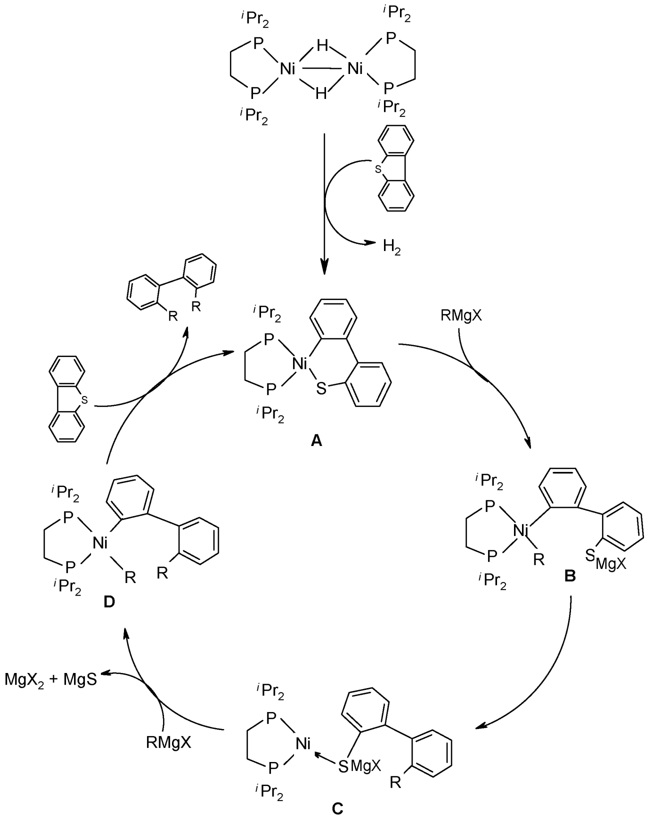
(17) ^{31}P{^{1}H} NMR signals in toluene-d_8 are for **4** δ 74.39 (d, $^2J_{P-P}$ 10 Hz); 75.55 (d, $^2J_{P-P}$ 10 Hz); for **5** δ 70.0 (s); for [(dippe)$_2$Ni] δ 54.5 (s); for [(dippe)$_2$Ni$_2$(μ-S)] δ 73.6 (d, $^2J_{P-P}$ 23 Hz); 77.8 (d, $^2J_{P-P}$ 23 Hz); for [(dippe)Ni(μ-S)]$_2$ δ 77.9 (s); for [(dippe)Ni(μ-S)]$_2$Ni(2,2′-biphenyl) δ 79.8 (s).

Scheme 1



of the reaction together with **5** and [(dippe)$_2$Ni]. None of the nickel−sulfur compounds remain in solution at the end of the reaction, consistent with the regeneration of Ni(0).

The final fate of sulfur was identified as MgS in a mixture with MgBr$_2$ by powder X-ray diffraction. Since both compounds were insoluble in toluene or THF, they precipitated during the reaction time as a beige precipitate mixed with red-brown powder. However, due to the overlap of some of the signals of both compounds, the solid mixture was hydrolyzed with concentrated hydrochloric acid to release H$_2$S, identified by its characteristic odor, and also by bubbling the released gases into a saturated aqueous solution of Pb(CH$_3$COO)$_2$ to yield PbS as a black precipitate, identified unambiguously by its powder X-ray pattern.[18]

According to the catalytic cycle generally accepted for the nickel-catalyzed cross-coupling reactions,[9,19] a mechanistic proposal for this process is depicted in Scheme 1.

We have demonstrated that mono- or diphosphino-containing Ni(0) complexes are efficient catalyst precursors for the desulfurization of the low reactive DBT, 4-MeDBT, and 4,6-Me$_2$DBT in the presence of alkyl Grignards to yield substituted biphenyls via cross-coupling reactions or HDS products such as biphenyl if a β-hydrogen is present in the alkyl group. In that regard we have shown that thiametallacycles are key intermediaries in both desulfurization processes. The final fate of sulfur is MgS, which upon acid hydrolysis releases H$_2$S. Studies are currently underway to extend the scope of this reaction to other transition metals and nucleophiles.

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Supporting Information Available: Experimental details, tables of complete cross-coupling experiments, and powder X-ray diffraction determinations (PDF). This material is available free of charge via Internet at http://pubs.acs.org.

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